



Molecular level insights to the interaction of toluene with ZrO_2 -based biomass gasification gas clean-up catalysts

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ABSTRACT

Gasification of biomass, followed by ZrO_2 -catalyzed hot gas clean-up at 600–900 °C for the oxidation of impurities (such as tar), is an environmentally attractive way to produce heat and power or synthesis gas. The interaction of toluene (as a model compound for tar) with ZrO_2 -based gasification gas clean-up catalysts was studied by in situ DRIFTS and temperature-programmed gas-phase analysis. Toluene was found to interact in four ways with ZrO_2 surfaces: forming molecularly adsorbed toluene, surface benzoate species, carbonaceous deposits and surface benzyl species. The adsorption of toluene in the absence of gas-phase oxygen at ambient temperature on ZrO_2 -based catalysts resulted in weakly adsorbed molecular toluene, while the adsorption of toluene at higher temperatures yielded carbonaceous deposits and surface benzoate species. Combined analysis of infrared and TP data showed that some of the benzoate species decomposed, producing benzene and carbon dioxide. Surface benzyl species, on the other hand, were detected on the surface of ZrO_2 -based catalysts only in the presence of gas-phase oxygen at a temperature where toluene and oxygen started to convert. Therefore, it is suggested that benzyl species are the active intermediates from toluene to carbon oxides during the gasification gas cleaning over ZrO_2 -based catalysts.

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1. Introduction

Gasification of biomass is a thermochemical process, which converts biomass into syngas (mixture of CO and H_2) [1]. The applications of the product gas include production of energy, H_2 , second generation liquid biofuels via Fischer–Tropsch synthesis and several chemicals. However, the product gas also contains impurities such as tar (aromatic hydrocarbons heavier than benzene), and therefore it has to be cleaned before use [2]. Hot-gas cleaning with a catalyst-coated monolith after biomass gasification is a preferable choice for tar decomposition [3]. Since the gas from the gasifier is a complex mixture of compounds, several decomposition and equilibrium reactions take place simultaneously during catalytic gas cleaning. Thus, the determination of tar decomposition reaction rates in the presence of other gas components, such as CO, H_2 , CO_2 or H_2O , is challenging [4].

Zirconia-based catalysts have shown to selectively oxidize tar molecules into CO and CO_2 during hot gas clean-up at 600–900 °C when a small amount of oxygen is added to the gas [5]. However, this addition of oxygen changes the tar decomposition

mechanism and makes the determination of tar decomposition reaction rates even more complicated. Furthermore, changes in the composition of the gas along the catalyst-coated monolith have been measured [4,6,7]. At the oxygen-rich zone in the inlet of the monolith, tar molecules preferably use the oxygen available and are oxidized mainly to CO and CO_2 . However, near the outlet of the monolith, oxygen is nearly or completely consumed, and therefore other reactions (such as steam and dry reforming, hydro-cracking, carbon formation, etc.) might be preferred. The activity of selected ZrO_2 -based catalysts in the decomposition of tar from synthetic gasification gas in the presence of oxygen (3 vol%) have been reported to decrease in the order of $\text{ZrO}_2 > \text{Y}_2\text{O}_3-\text{ZrO}_2 > \text{SiO}_2-\text{ZrO}_2$ [7].

Certain physical and chemical properties have been related to the tar decomposition activity of ZrO_2 -based gasification gas clean-up catalysts [5,7]. For example, Juutilainen et al. suggested that increased acidity is not favorable for ZrO_2 -based gasification gas cleaning catalyst [5]. In contrast to the high total amount and strength of acidic surface sites, the high total amount and strength of basic surface sites seem to be essential for an active ZrO_2 tar decomposition catalyst [7]. Furthermore, the combination of suitable redox properties of ZrO_2 -based gasification gas clean-up catalysts as well as their tendency to generate oxygen vacancies has been related to high activity in tar decomposition [7].

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Table 1

The specific surface areas as well as the amounts of basic and acidic surface sites of the ZrO_2 -based catalysts [7].

Catalyst	Specific surface area (m^2/g)	Amount of basic sites ($\mu\text{mol/g}$)	Amount of acidic sites ($\mu\text{mol/g}$)
ZrO_2	24	84	22
$\text{Y}_2\text{O}_3\text{-ZrO}_2$	53	146	36
$\text{SiO}_2\text{-ZrO}_2$	92	49	78

Molecular level insight into the ZrO_2 -based catalysts under gasification gas conditions offers essential information needed, e.g. when optimizing the catalyst composition. Furthermore, such knowledge combined with the understanding of the influence of gas components on the catalyst performance allows the design and optimization of the cleaning process to ensure high-quality product gas. Since the gasification gas is a complex matrix, a novel approach is needed for overcoming the challenge of finding the tar decomposition mechanism. Our approach is to diminish the complexity by studying simpler subsystems with fewer components and fewer reactions at a time. The first step in this approach is to understand the interaction of a single tar component with ZrO_2 -based catalysts. Later the complexity is increased by adding components one by one. By combining *in situ* spectroscopic methods with temperature-programmed gas-phase analysis, unique knowledge on the relevant surface species and reaction mechanisms is obtained. In this study the adsorption of toluene (as a model compound for tar) is investigated to obtain an insight into toluene decomposition during gasification gas cleaning.

The adsorption of toluene has been studied widely over various reducing and non-reducing oxide catalysts [8–17]. However, the mechanism with which toluene interacts with ZrO_2 -based gasification gas clean-up catalysts has not yet been established. Therefore, the adsorption of toluene over selected ZrO_2 -based catalysts was studied at temperatures from 30 °C to as high as 600 °C, 600 °C being the relevant temperature for hot-gas cleaning. A reduction pretreatment was applied to the catalysts in order to reduce the amount of surface hydroxyl groups on the catalyst to imitate the reducing conditions of the gasification gas (gasification gas always contains hydrogen and CO). The aim of this study was to discover the relevant surface species formed from toluene in the absence and presence of gas-phase oxygen as well as to estimate the decomposition mechanism of the adsorbed toluene-derived species over ZrO_2 , $\text{Y}_2\text{O}_3\text{-ZrO}_2$ and $\text{SiO}_2\text{-ZrO}_2$.

2. Experimental

Pure ZrO_2 , 5 mol% $\text{Y}_2\text{O}_3\text{-ZrO}_2$, and 8 mol% $\text{SiO}_2\text{-ZrO}_2$ were provided by MEL Chemicals, where $\text{Y}_2\text{O}_3\text{-ZrO}_2$ and $\text{SiO}_2\text{-ZrO}_2$ were prepared by co-precipitation. The catalysts were calcined in static air at 800 °C for 1 h. The specific surface areas as well as the amounts of basic and acidic surface sites of the catalysts are shown in Table 1. Other previously measured physical and chemical properties of the catalysts have been reported elsewhere [7,18]. Two complementary techniques were used to study the interaction of toluene with ZrO_2 -based gasification gas clean-up catalysts: *in situ* DRIFTS and temperature-programmed gas-phase analysis. Three types of experiments were carried out with both techniques: (1) temperature-programmed desorption of toluene (TPD), (2) temperature-programmed adsorption of toluene (TPA), and (3) temperature-programmed oxidation of adsorbed surface species (TPO). The feed gas compositions and heating rates were matched as close as possible in the DRIFTS and TPA gas-phase analysis in order to guarantee accurate comparison between surface species and gas-phase products. This allows surface phenomena to be linked with gas-phase composition. In addition, the interaction of toluene and

oxygen over ZrO_2 -based catalysts was studied via the temperature-programmed surface reaction between toluene and oxygen (TPSR) using only *in situ* DRIFTS. Toluene was chosen as a model compound for tar.

2.1. *In situ* DRIFTS experiments

In situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) measurements were performed with a Nicolet Nexus FTIR spectrometer and a Spectra-Tech high temperature/high pressure chamber. The total gas flow through the reaction chamber (passing over the catalyst sample) was kept at 50 cm^3/min throughout the experiments. A catalyst sample powder (approx. 30 mg) was pretreated by *in situ* calcination with 10% O_2/N_2 (synthetic air 99.99%, N_2 99.999%, AGA) at 600 °C for 2 h followed by N_2 flush for 1 h. In all experiments, the spectrum of an aluminum mirror measured (4 cm^{-1} resolution, 200 scans) under nitrogen flow was used as the background. After the calcination, the catalyst sample was pre-reduced with 5% H_2/N_2 (H_2 99.999%, AGA) at 600 °C for 15 min. Spectra were recorded every minute (4 cm^{-1} , 30 scans) for the first 8 min on stream and then after 9 and 12 min (4 cm^{-1} , 100 scans). After the reduction, the catalyst sample was flushed with nitrogen for 30 min while cooling down to the adsorption temperature of toluene.

In the TPD experiments, toluene (750 ppm toluene in He with 1–2 ppm water and even smaller amount of methanol as impurities, AGA) was fed to the sample cell at 30 °C and in the TPA experiments at 100 °C for 30 min. Spectra were collected once every minute (4 cm^{-1} , 30 scans) for the first 5 min, and thereafter once every 5 min (4 cm^{-1} , 100 scans). After the adsorption of toluene, the samples were flushed with nitrogen for 30 min to obtain spectra without the contribution of gas-phase toluene. In the TPD experiments, desorption of the adsorbed species from the samples was followed with increasing temperature stepwise from 30 to 600 °C. During the heating of the sample, spectra (4 cm^{-1} , 100 scans) were collected every 25 °C, i.e. every 4 min. In the TPA experiments, toluene flow was directed back to the sample cell after the nitrogen flush at 100 °C and temperature was increased stepwise from 100 to 200 °C. At 200 °C, the sample cell was flushed with nitrogen for 5 min and a spectrum (4 cm^{-1} , 100 scans) was recorded. In the TPA experiments, spectra (4 cm^{-1} , 100 scans) were collected every 25 °C, i.e. every 5 min under toluene flow and additionally at 100, 200, 300, 400, 500 and 600 °C under nitrogen flow. For comparison, an additional TPA experiment was performed using a calcined ZrO_2 sample, i.e. without hydrogen pre-reduction.

In the TPO experiments, toluene was adsorbed at 600 °C for 30 min and then the sample was flushed with nitrogen while cooling down to 30 °C. Next, the adsorbed species were oxidized (2% O_2/N_2) with increasing temperature stepwise from 30 to 600 °C while spectra (4 cm^{-1} , 100 scans) were collected every 25 °C, i.e. every 5 min.

In the TPSR experiments, 45 cm^3/min toluene (750 ppm in He) and 5 cm^3/min N_2 (yielding a gas mixture of 675 ppm toluene, 90% He and 10% N_2) was first fed to the sample at 100 °C for 1 h. Thereafter N_2 was replaced by synthetic air, resulting in a gas mixture of 675 ppm toluene, 90% He, 2% oxygen and 8% N_2 . The oxygen concentration in the TPSR experiments was kept as low as possible but still resulting in an oxygen surplus, thus matching the oxygen feed composition in the gasification gas cleaning. After a 30-min stabilizing period, the sample cell was heated in the toluene-helium-air mixture from 100 to 600 °C. The spectra (4 cm^{-1} , 100 scans) were collected every 25 °C, i.e. every 5 min. The gas flow from the reactor in the TPSR experiments was followed with a Pfeiffer Vacuum Omnistar mass spectrometer. It should be noted that accurate kinetic data cannot be obtained because there

is not a well-defined contact between the gas flow and the catalyst bed.

2.2. Temperature-programmed gas-phase analysis

Temperature-programmed (TP) gas-phase analysis was applied to study in detail the gas-phase products during adsorption of toluene. TP gas-phase analyses were designed to mimic the DRIFTS experiments. However, when preparing the samples, the powder samples were first pressed into pellets. Furthermore, to obtain the desired particle size of 0.25–0.42 mm, the pellets were crushed and sieved. The sample amount used in the experiments was 0.1 g. TP experiments were carried out in an Altamira AMI-100 characterization system. Prior to the experiments, a similar pre-treatment method was applied as in the DRIFTS experiments: the samples were calcined *in situ* in O₂/He flow of 50 cm³/min (5 vol% O₂ in He, AGA) at 600 °C for 2 h, and reduced in 5 vol% H₂/He for 15 min (H₂ 99.999%, AGA). Gaseous products were analyzed with a mass spectrometer (MS, OmniStar GSD320, Pfeiffer Vacuum). The *m/z* values monitored in each experiment were 2 (H₂), 4 (He), 15 (CH₄), 16 (O₂), 18 (H₂O), 28 (CO), 32 (O₂), 44 (CO₂), 65 (toluene), 78 (benzene), 91 (toluene), 92 (toluene), 106 (benzaldehyde), 108 (benzyl alcohol) and 122 (benzoic acid).

The TPD experiments were similar to the corresponding DRIFTS experiments: first toluene (750 ppm in He with 1–2 ppm water and even smaller amount of methanol as impurities, AGA) with a flow of 49 cm³/min was fed to the samples at ambient temperature for 30 min, then the reactor was flushed with a flow of 50 cm³/min of He (99.996%, AGA) for 30 min and a TPD experiment was performed under the same He flow with a temperature ramp from ambient temperature to 600 °C (at the rate of 10 °C/min). The desorbed toluene amounts were quantified. Toluene-derived species possibly remaining on the ZrO₂ surface after the TPD heat ramp was investigated by TPO. The results showed no significant amounts of CO₂, and therefore it could be concluded that no toluene remained on the surface after desorption at 600 °C. A blank TPD experiment was performed on Y₂O₃–ZrO₂ to follow the formation of gas-phase products from the catalyst surface without toluene adsorption.

The TPA and TPO experiments were carried out in the same test cycle: first TPA followed by TPO, thus slightly differing from the corresponding DRIFTS experiments. During the TPA, a total flow of 49 cm³/min of a gas mixture containing toluene (750 ppm in He, AGA) was passed through the sample first at ambient temperature for 30 min. Thereafter, a temperature ramp was applied under the same toluene flow (ambient to 600 °C, 10 °C/min). The toluene and possible products from its reactions (CO₂, CO, H₂, H₂O, benzene) during adsorption with increasing temperature were recorded with MS. Toluene flow was kept constant at 600 °C for 15 min, after which the reactor was flushed with a He flow of 50 cm³/min for 30 min and cooled down to 30 °C to start the TPO experiment.

The TPO experiment was carried out from ambient temperature to 600 °C (ramp rate 10 °C/min) under a gas mixture of 25 cm³/min O₂/He (5 vol%) and 25 cm³/min He, resulting in a total flow of 50 cm³/min and an oxygen content of 2.5 vol%. The sample was let to dwell at 600 °C for 30 min. The consumption of oxygen and the formation of oxidation products (CO₂, CO, H₂, and H₂O) were monitored with MS. The possible formation of oxygen containing benzene derivatives was monitored (*m/z* values of 106, 108, and 122), but these species were not observed.

3. Results

The nature of adsorbed toluene species in the absence and presence of gas-phase oxygen was studied in order to evaluate their interaction over ZrO₂-based gasification gas clean-up catalysts.

Toluene TPD was studied to discover the surface species formed upon the adsorption of toluene at low temperature and to evaluate their thermal stability. Toluene TPA was studied to follow the evolution of surface species and gas-phase products as a function of temperature in the absence of gas-phase oxygen. TPO of the toluene-derived surface species was studied to determine their reactivity toward oxygen. TPSR between toluene and oxygen was studied to discover additional surface species during toluene oxidation.

3.1. Temperature-programmed desorption of toluene (TPD)

3.1.1. Surface species during toluene TPD

Toluene adsorption at 30 °C produced several peaks in the spectra of ZrO₂, Y₂O₃–ZrO₂, and SiO₂–ZrO₂ (all the vibrations and their assignments are collected in Table 2). The spectra of pure ZrO₂ in the region of 3200–2600 cm^{−1} recorded during the toluene TPD experiment are shown in Fig. 1a. Small peaks at 3030, 2926, 2818, 1601, and 1492 cm^{−1} remained in the spectrum after toluene adsorption and nitrogen flush at 30 °C. The peak at 3030 cm^{−1} can be assigned to the C–H stretching modes of the aromatic ring of toluene and the peaks at 1601 and 1492 cm^{−1} (Fig. S1a in Supplementary data) to the skeleton vibrations of the aromatic ring of toluene [19]. The peak at 2926 cm^{−1} could be assigned to ν (CH) modes of the methyl group of toluene [19] but the lower intensity compared to that of peak at 3030 cm^{−1} suggests that this assignment is unlikely. Therefore, the small peaks at 2926 and 2818 cm^{−1} are assigned to impurity-originated (trace amount of CH₃OH was analyzed from the feed) methoxy species together with the small peaks at 1153 and 1057 cm^{−1} (not shown) [18,20].

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The spectra of Y₂O₃–ZrO₂ and SiO₂–ZrO₂ in the region of 3200–2600 cm^{−1} collected during the toluene TPD experiments are shown in Fig. 1b and c, respectively. The number of peaks in the spectra of both Y₂O₃–ZrO₂ and SiO₂–ZrO₂ was higher compared to that of pure ZrO₂ after the nitrogen flush. Furthermore, the intensity of the peaks in the spectra of SiO₂–ZrO₂ was greater than in the spectra of the other catalysts. The peaks in the spectra of Y₂O₃–ZrO₂ and SiO₂–ZrO₂ at ca. 3080, 3060 and 3030 cm^{−1} can be assigned to the C–H stretching modes of the aromatic ring of toluene, and the bands at ca. 1600 and 1495 cm^{−1} (Fig. S1b and c in Supplementary data) to the skeleton vibrations of the aromatic ring of toluene [19]. The peak at ca. 1600 cm^{−1} in the spectrum of SiO₂–ZrO₂ was evidently much stronger and broader than the other peaks in the spectra. However, the assignment of this peak is unclear. In addition, the peaks at ca. 1450 and 1380 cm^{−1} over Y₂O₃–ZrO₂ and SiO₂–ZrO₂ (Fig. S1b and c in Supplementary data) can be assigned to the asymmetric and symmetric bending modes of the methyl group [19], while the bands at ca. 2925 and 2880 cm^{−1} can be assigned to ν (CH) modes of the methyl group of toluene [19]. Furthermore, a small peak at 1177 cm^{−1} in the spectra of Y₂O₃–ZrO₂ suggests that methoxy species might also be present [18]. In addition, a peak at ca. 1420 cm^{−1} in the spectra of the doped zirconias (Fig. S1b and c in Supplementary data) could refer to surface carbonates together with the peak at ca. 1450 cm^{−1}.

In addition, the peak at ca. 3770 cm^{−1} (not shown) in the spectrum of ZrO₂ and Y₂O₃–ZrO₂, previously assigned to terminal OH groups of ZrO₂ [7], disappeared during the adsorption of toluene, whereas a relatively broad peak appeared at ca. 3575 cm^{−1}. Similar results were obtained by Hernández-Alonso et al. [19], who suggested that the peak at ca. 3575 cm^{−1} indicates that the adsorption of toluene occurs via hydrogen bonding on the isolated (terminal) OH groups of the catalyst surface. Furthermore, some water entered as a minor impurity in the toluene/He mixture and accumulated on the surface of ZrO₂-based catalysts, thereby produced an extremely

Table 2Vibrations and assignments of IR peaks appearing in the spectra of ZrO_2 -based catalysts in toluene adsorption experiments.

Vibrations	Assignment	References
3770	Terminal OH-groups	[7,17]
3575	Hydrogen-bonded OH stretching vibration	[19]
3085, 3055, 3025	Molecularly adsorbed toluene (C—H stretching vibrations of the aromatic ring)	[19]
3070	C—H stretching vibrations of the aromatic ring	[15]
2960, 2880	Benzyl species (C—H stretching vibrations of CH_2 group)	[21]
2925, 2880	Molecularly adsorbed toluene (C—H stretching vibrations of the methyl group)	[19]
2925, 2820, 1153, 1057	Methoxy species (CH_3 and $\text{O}-\text{CH}_3$ vibrations)	[18,20]
2880, 1563, 1443, 1365	Formate species (C—H and COO vibrations)	[18,20]
1600, 1580, 1495	Molecularly adsorbed toluene (skeletal vibrations of the aromatic ring)	[19]
1510, 1410	Benzoate species (COO vibrations)	[8,15]
1450, 1370	Molecularly adsorbed toluene (bending vibrations of the methyl group)	[19]
1440, 1430	Monodentate carbonates ^a on Y_2O_3 -doped ZrO_2	[7,22]
1440, 1430	Polydentate carbonates ^a on SiO_2 -doped ZrO_2	[7,17]

^a The assignments of monodentate and polydentate carbonates on doped zirconias are based on the thermal stability of these species. Further details can be found in [7].

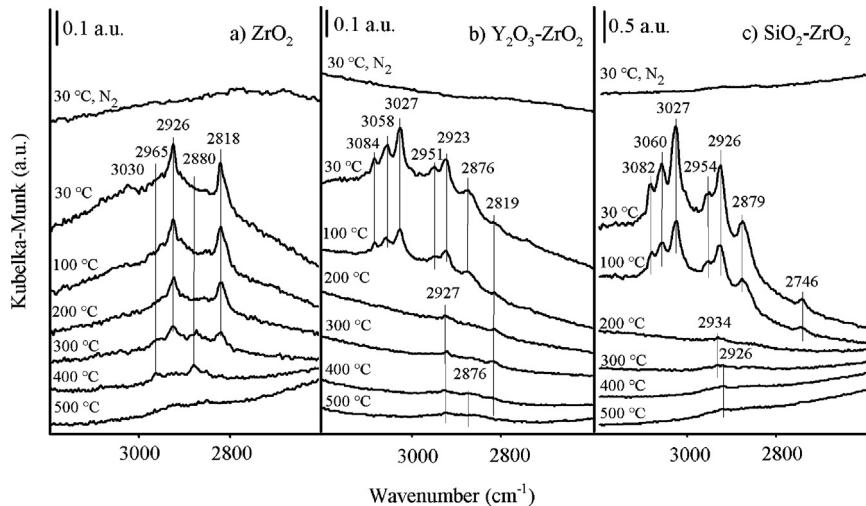


Fig. 1. DRIFTS spectra from the TPD experiments in the region of 3200–2600 cm^{-1} of calcined and reduced (a) ZrO_2 , (b) Y_2O_3 – ZrO_2 and (c) SiO_2 – ZrO_2 after toluene adsorption at 30 °C followed by heating in nitrogen from 30 to 500 °C.

broad peak in the spectra of all the catalysts across the range of interest.

Upon heating the samples after the adsorption of toluene and the nitrogen flush (Fig. 1), the peaks assigned to molecular toluene vanished from the spectra of all of the ZrO_2 -based catalysts at temperatures below 200 °C, indicating desorption of adsorbed molecular toluene. Small new peaks at 2880, 1563, 1443 and 1365 cm^{-1} appeared at 225 °C to the spectrum of pure ZrO_2 , suggesting that small amounts of formate species might be present. Methoxy species observed over pure ZrO_2 desorbed at 400 °C, while the formate species desorbed at 425 °C, in accordance with methanol adsorption experiments in the literature [18,20]. During the heat ramp, the terminal OH groups of the surface of the ZrO_2 -based samples were restored (not shown).

3.1.2. Gas-phase products during toluene TPD

The gas-phase products during adsorption of toluene ($m/z = 91$) at ambient temperature followed by desorption with heating up to 600 °C were studied over the ZrO_2 -based catalysts. Fig. 2 shows the adsorption of toluene and the following TPD. All the ZrO_2 -based catalysts were able to adsorb toluene. The lowest amount of toluene was adsorbed on pure ZrO_2 and the highest amount on SiO_2 -doped ZrO_2 . This is shown in Fig. 2, where the signal of toluene on ZrO_2 levels off first, indicating that this sample is saturated with toluene sooner than the doped zirconias. It appears that desorption of toluene was taking place already during the isothermal inert flush, but it accelerated with heating. The inset

in Fig. 2 shows the temperature dependence of toluene desorption peaks. The temperatures of the desorption rate maxima (T_{\max} , °C) of toluene over ZrO_2 , Y_2O_3 – ZrO_2 and SiO_2 – ZrO_2 were 70, 80, and 88 °C, respectively. The amount of desorbed toluene per area of catalyst on ZrO_2 , Y_2O_3 – ZrO_2 , and SiO_2 – ZrO_2 was calculated to be approximately 0.13, 0.23, and 0.23 $\mu\text{mol}/\text{m}^2_{\text{cat}}$, corresponding to less than 4% of a monolayer.

In addition to toluene, trace amounts of CO_2 and CO were detected on all the catalysts during TPD (not shown). A blank TPD experiment, i.e. without toluene adsorption, showed no CO_2 evolution from Y_2O_3 – ZrO_2 . The formation of carbon oxides in toluene TPD experiments has also been observed by Saeer et al. [23] over Al_2O_3 -supported metal oxide catalysts. They related the formation of CO_2 to the reduction of the catalyst surface and to the activity of surface oxygen [23]. ZrO_2 -based catalysts in this work, on the other hand, were pretreated by hydrogen reduction and therefore were expected to possess only a minor redox capacity. Thus it is expected that trace amount of feed-originated methanol (or CO_2) was retained on the surface as carbonates (in accordance with ref [18]) that were detected in the DRIFTS spectra (Section 3.1.1) and subsequently released at characteristic temperatures.

Furthermore, significant amounts of water desorbed during TPD from all the catalysts. The T_{\max} values (°C) of the H_2O desorption curves were 290 °C (ZrO_2), 340 °C (Y_2O_3 – ZrO_2) and 385 °C (SiO_2 – ZrO_2). A blank TPD experiment (without toluene adsorption) on Y_2O_3 – ZrO_2 indicated a minor desorption process of water with similar qualitative characteristics in similar temperature range

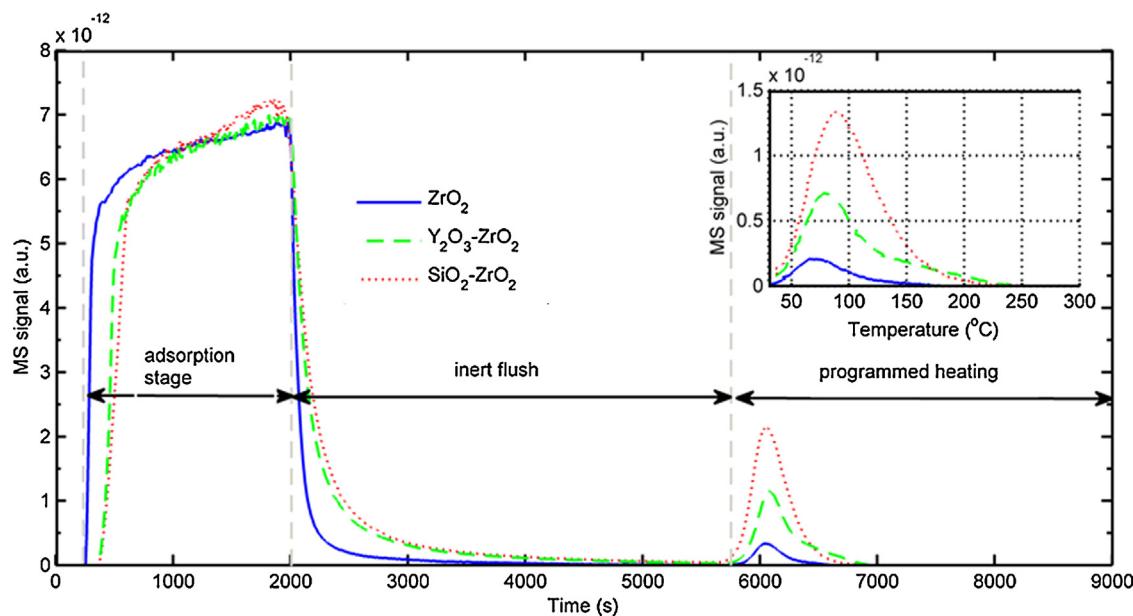


Fig. 2. Toluene adsorption at ambient temperature followed by desorption to 600 °C over ZrO_2 , $\text{Y}_2\text{O}_3\text{-ZrO}_2$ and $\text{SiO}_2\text{-ZrO}_2$. The inset shows the toluene desorption peaks as a function of temperature.

(~250–450 °C). Therefore, the desorption of water during TPD is likely related to dehydroxylation of the ZrO_2 surfaces at these temperatures. For example, Bianchi et al. [24] connected water formation during methanol TPD over ZrO_2 to dehydroxylation of the surface, where two hydroxyl groups are combined to yield water in the gas phase. The water evolution in the toluene TPD was tenfold in amount compared to the blank TPD. This is explained by more extensive hydroxylation of zirconia caused by water that entered as a minor impurity in the toluene/He mixture and its accumulation on the catalyst during the preceding adsorption stage.

3.2. Temperature-programmed adsorption of toluene (TPA)

3.2.1. Surface species during toluene TPA

In the TPA experiments, toluene adsorption on the calcined and hydrogen reduced ZrO_2 , $\text{Y}_2\text{O}_3\text{-ZrO}_2$ and $\text{SiO}_2\text{-ZrO}_2$ samples was studied in the temperature range of 100 to 600 °C. The spectra in the range of 1700–1300 cm^{-1} are shown in Fig. 3 for all of the catalysts. Toluene adsorption at 100 °C was similar to the adsorption of toluene at 30 °C. Several peaks appeared in the spectra of all the ZrO_2 -based catalysts, the peak assigned to the terminal OH groups (at ca. 3770 cm^{-1}) disappeared, and a broad peak at 3575 cm^{-1} appeared (not shown). Small peaks at 2928 (Fig. S2a in Supplementary data) and 1489 cm^{-1} (Fig. 3a) remained in the spectrum of pure ZrO_2 during nitrogen flush after the adsorption of toluene at 100 °C. The peak at 2928 cm^{-1} can be assigned to $\nu(\text{CH})$ modes of the methyl group [19], and the peak at 1490 cm^{-1} can be assigned to the skeleton vibrations of the aromatic ring of toluene [19].

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The number of peaks after adsorption of toluene at 100 °C was again higher in the spectra of both $\text{Y}_2\text{O}_3\text{-ZrO}_2$ (Fig. 3b) and $\text{SiO}_2\text{-ZrO}_2$ (Fig. 3c) compared to that of pure ZrO_2 (Fig. 3a). The peaks in the spectra of $\text{Y}_2\text{O}_3\text{-ZrO}_2$ and $\text{SiO}_2\text{-ZrO}_2$ at ca. 3080, 3060, 3030, 2925 (Fig. S2b and c in Supplementary data), 1600, 1495, and 1450 cm^{-1} can be assigned to the adsorption of molecular toluene similar to the adsorption at 30 °C (Fig. 1). Similarly to the TPD experiments, the peak at ca. 1600 cm^{-1} in the spectrum of $\text{SiO}_2\text{-ZrO}_2$ was much stronger and broader than the other peaks in the spectra. The assignment of this peak remains unclear. In addition, a peak

at ca. 1420 cm^{-1} appeared in the spectra of both $\text{Y}_2\text{O}_3\text{-ZrO}_2$ and $\text{SiO}_2\text{-ZrO}_2$. The strong bands at ca. 1450 and 1420 cm^{-1} have been previously assigned to the adsorbed CO_2 species [7]. The existence of these carbonate species is related to the feed-originated minor CH_3OH impurity in accordance with the results of the gas-phase analysis during the toluene TPD experiments (Section 3.1.2).

Heating under toluene flow from 100 to 600 °C resulted in the appearance of new peaks at temperatures above 300 °C in the spectra of pure ZrO_2 (Fig. 3a) at ca. 3070 (Fig. S2a in Supplementary data), 1580, 1510, and 1410 cm^{-1} . The intensity of these new peaks increased with increasing temperature. The peaks at ca. 1510 and 1410 cm^{-1} can be assigned to asymmetric and symmetric stretching modes of adsorbed benzoate species, whose presence indicate that the C-H bonds in the methyl group of toluene can dissociate [8]. First hydrogen is abstracted from the methyl group of toluene and a surface benzoate is formed with two surface oxygen atoms of the catalyst [8]. In addition, the bands appearing at 3070 and 1585 cm^{-1} can be assigned to the skeleton vibrations of the aromatic ring of benzoate species [8,19]. The peaks at 1540 and 1340 cm^{-1} are original peaks of the ZrO_2 sample. The reference TPA experiment on calcined ZrO_2 showed the same surface species as on the calcined and reduced ZrO_2 : molecularly adsorbed toluene at low temperatures and benzoate species at higher temperatures. However, the amount of benzoate species was higher on the calcined than on the calcined and reduced ZrO_2 surface, which seems logical because the calcined sample has more oxygen available on the surface of the catalyst.

In the spectra of $\text{Y}_2\text{O}_3\text{-ZrO}_2$ (Fig. 3b), peaks at 3080, 3060, 3030 (Fig. S2b in Supplementary data), 1600, and 1494 cm^{-1} vanished below 300 °C, the peak at 1447 cm^{-1} remained in the spectra throughout the temperature range, and the intensity of the peak at 1420 cm^{-1} grew with increasing temperature. In addition, a new band at ca. 3070 cm^{-1} (Fig. S2b in Supplementary data), which can be assigned to C-H stretching of the aromatic ring [15], appeared to the spectrum of $\text{Y}_2\text{O}_3\text{-ZrO}_2$ at temperatures above 400 °C. Previously, bands at ca. 1450 and 1420 cm^{-1} (which vanish below 500 °C) have been assigned to monodentate carbonates formed in the adsorption of CO_2 to the surface of $\text{Y}_2\text{O}_3\text{-ZrO}_2$ [7]. Therefore, the thermal stability of the peaks suggests that at lower temperatures, the peaks at 1447 and 1418 cm^{-1} can be assigned to monodentate

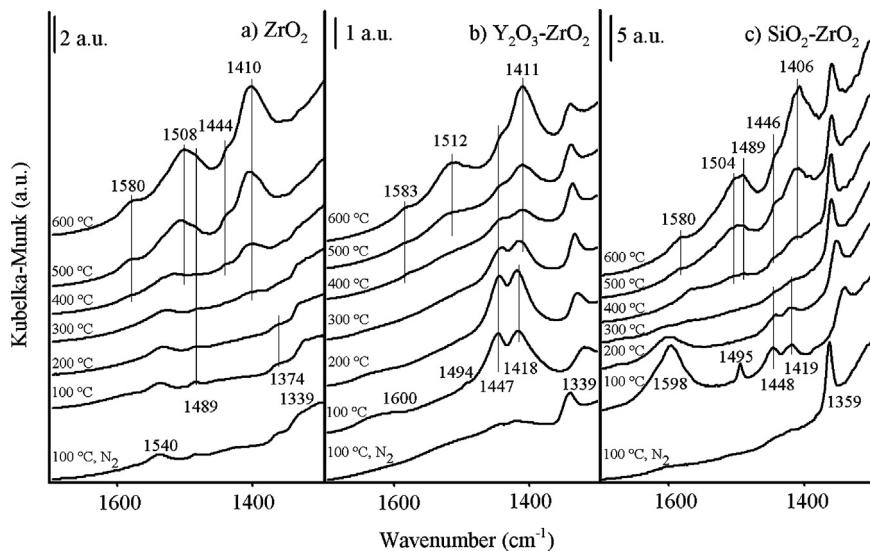


Fig. 3. DRIFTS spectra from the TPA experiments in the region of 1700–1300 cm^{-1} of calcined and reduced (a) ZrO_2 , (b) $\text{Y}_2\text{O}_3\text{-ZrO}_2$ and (c) $\text{SiO}_2\text{-ZrO}_2$ during toluene adsorption at 100–600 $^{\circ}\text{C}$. Spectra recorded after a 5-min nitrogen flush at each temperature.

carbonates [7], and at higher temperatures the peak at 1418 cm^{-1} can be assigned to the benzoate species together with the increasing peak at 1512 cm^{-1} , which is first detected at 400 $^{\circ}\text{C}$ [8]. The peak at 1339 cm^{-1} is an original peak of the $\text{Y}_2\text{O}_3\text{-ZrO}_2$ sample.

In the spectra of $\text{SiO}_2\text{-ZrO}_2$ (Fig. 3c), the peak at 1495 cm^{-1} vanished below 200 $^{\circ}\text{C}$ and the peaks at 3080, 3060, and 3030 cm^{-1} below 300 $^{\circ}\text{C}$ (Fig. S2c in Supplementary data), while the peaks at 1598, 1448, and 1419 cm^{-1} vanished above 300 $^{\circ}\text{C}$. New peaks appeared in the spectra of $\text{SiO}_2\text{-ZrO}_2$ at 3070, 1504, and 1406 cm^{-1} above 300 $^{\circ}\text{C}$. The peaks appearing at lower temperatures (1448 and 1419 cm^{-1}) can be assigned to polydentate carbonates formed by the adsorption of CO_2 to the surface of $\text{SiO}_2\text{-ZrO}_2$ in accordance with our previous findings (monodentate carbonates on $\text{Y}_2\text{O}_3\text{-ZrO}_2$ and polydentate carbonates on $\text{SiO}_2\text{-ZrO}_2$) [7] and the increasing peaks appearing at higher temperatures (1504 and 1406 cm^{-1}) to benzoate species [8]. In addition, the peak at 3070 cm^{-1} can be assigned to C-H stretching of the aromatic ring of benzoate [15]. The peak 1359 cm^{-1} is an original peak of the $\text{SiO}_2\text{-ZrO}_2$ sample.

3.2.2. Gas-phase products during toluene TPA

The formation of gas-phase products from toluene over zirconia-based catalysts was followed from ambient temperature to 600 $^{\circ}\text{C}$ and thereafter during isothermal hold under toluene flow at the end temperature for 30 min. In the beginning of the experiment, the toluene feed was switched on and toluene adsorption on the catalysts continued until adsorption equilibrium was reached. Immediately when the heating was started, the net desorption of toluene began as the toluene outlet flow level rose above the toluene feed level. As an example, Fig. 4 shows the TPA response of toluene as a function of time with ZrO_2 and illustrates the net desorption peaks for all the catalysts as a function of temperature. The toluene desorption peaks in the TPA experiments were more intense than in the TPD experiments, suggesting that during the inert flush prior to the TPD a fraction of toluene was lost. The temperature range of the net desorption of toluene in the TPA was lower with all of the catalysts (T_{max} values 30, 55, and 40 $^{\circ}\text{C}$ for ZrO_2 , $\text{Y}_2\text{O}_3\text{-ZrO}_2$, and $\text{SiO}_2\text{-ZrO}_2$, respectively) compared to the TPD experiments as well. The toluene net desorption amounts were 1.42, 1.23, and 0.82 $\mu\text{mol}/\text{m}_\text{cat}^2$ over ZrO_2 , $\text{Y}_2\text{O}_3\text{-ZrO}_2$, and $\text{SiO}_2\text{-ZrO}_2$, respectively. Interestingly, the toluene net desorption amount was highest over ZrO_2 in contrast to the toluene desorption amounts in the TPD experiments. All of the toluene net desorption

amounts were higher than in the TPD experiments because the lack of inert flush before the heating was started in the TPA experiments. After the net desorption peaks, toluene response returned to the feed level and remained there until almost the end of the temperature ramp. During the isothermal hold at 600 $^{\circ}\text{C}$, toluene was moderately consumed over pure ZrO_2 and $\text{Y}_2\text{O}_3\text{-ZrO}_2$ and less over $\text{SiO}_2\text{-ZrO}_2$.

The responses of components other than toluene were similar to those observed during toluene TPD. The most striking difference between the TPD and the TPA of toluene was the formation of benzene accompanied by CO_2 formation at 520–530 $^{\circ}\text{C}$ in the TPA. Fig. 5 shows the responses of CO_2 and benzene in detail. CO_2 formation was observed around two temperatures over all the studied catalysts. Small peaks for CO_2 were first detected at temperatures of 300–350 $^{\circ}\text{C}$ as in the TPD experiments (Section 3.1.2) and can be related to a feed-originated minor (CH_3OH) impurity. A maximum for CO_2 at high temperature (525 $^{\circ}\text{C}$ for ZrO_2 and $\text{Y}_2\text{O}_3\text{-ZrO}_2$, or 530 $^{\circ}\text{C}$ for $\text{SiO}_2\text{-ZrO}_2$) was common for all catalysts and was accompanied by the formation of benzene (C_6H_6) at the same temperatures. Furthermore, the estimated molar amounts of CO_2 and benzene desorbing at around 530 $^{\circ}\text{C}$ were approximately equivalent ($\sim 0.1 \mu\text{mol}/\text{m}^2$ for $\text{Y}_2\text{O}_3\text{-ZrO}_2$). The intensities of both CO_2 and benzene peaks decreased in the order of $\text{Y}_2\text{O}_3\text{-ZrO}_2 > \text{ZrO}_2 > \text{SiO}_2\text{-ZrO}_2$, which is interestingly the same order as the order of basicity on these catalysts [7]. Over ZrO_2 and $\text{Y}_2\text{O}_3\text{-ZrO}_2$, the formation of CO_2 , benzene (Fig. 5), and CO (not shown) increased after 550 $^{\circ}\text{C}$. These signals continued to increase even after 600 $^{\circ}\text{C}$ was reached (not shown) simultaneously with toluene consumption.

Moreover, some H_2 was produced (Fig. 5) at high temperature (approx. 500 $^{\circ}\text{C}$) over pure ZrO_2 and $\text{Y}_2\text{O}_3\text{-ZrO}_2$. However, the formation of H_2 increased (Fig. 5) considerably when toluene feed was continued at 600 $^{\circ}\text{C}$ for 30 min over all the studied catalysts. The increasing H_2 amount in the gas phase might be related to dehydrogenation of toluene forming carbonaceous deposits on the catalyst surface and, moreover, the exponential shape suggests that this is autocatalytic. Carbon formation has been suggested to occur during gasification gas cleaning via hydrocarbon decomposition reactions producing H_2 and carbon on the catalyst by Simell et al. [3]. Water was produced during the TPA experiments over ZrO_2 , $\text{Y}_2\text{O}_3\text{-ZrO}_2$, and $\text{SiO}_2\text{-ZrO}_2$ around 310, 375, and 400 $^{\circ}\text{C}$, respectively (Fig. 5). The H_2O T_{max} values ($^{\circ}\text{C}$) were similar to the TPD experiments

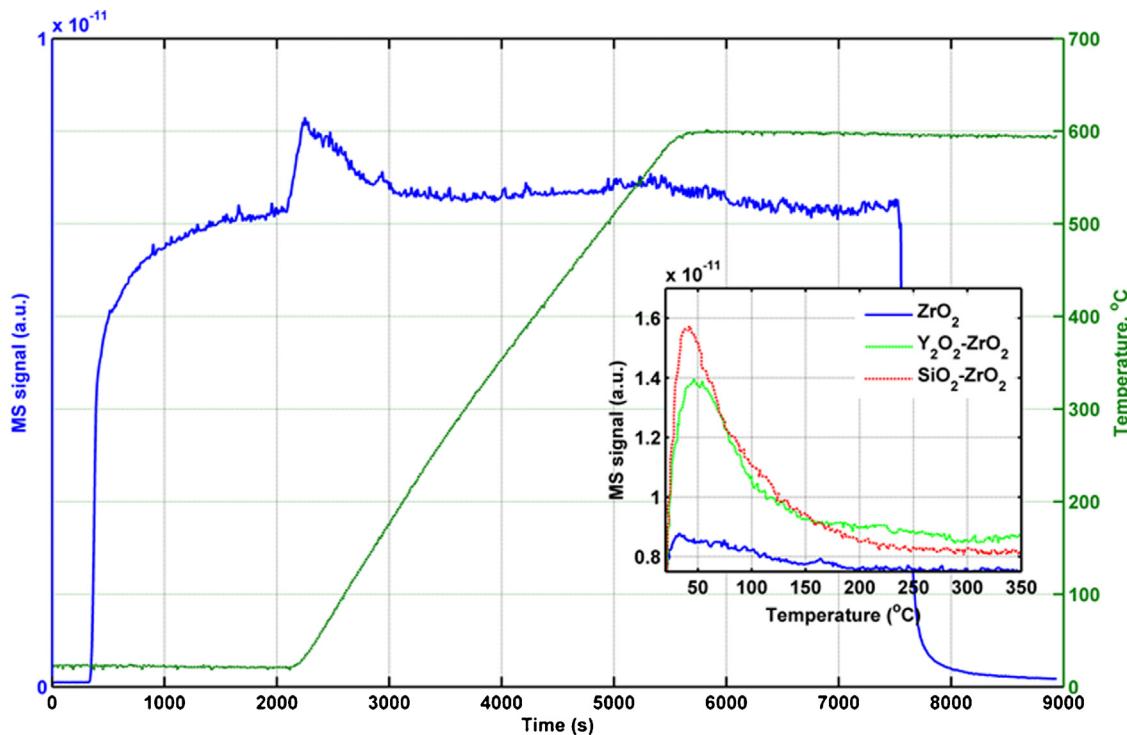


Fig. 4. Toluene response for ZrO_2 in TPA: toluene/He flow switched on at 20 °C, followed by constant heating and isothermal hold at 600 °C. The inset shows the temperature dependence of toluene desorption peaks over all the ZrO_2 -based catalysts.

(Section 3.1.2) and the origin of desorbing water is related here as well to the water that entered as a minor impurity in the toluene/He mixture and causing further hydration of the ZrO_2 surfaces.

3.3. Temperature-programmed oxidation of adsorbed toluene species (TPO)

3.3.1. Surface species during toluene TPO

In the TPO experiments, toluene was adsorbed at 600 °C for 30 min and ZrO_2 -based catalyst samples were flushed with nitrogen while cooling down to 30 °C. Next, the oxidation of the adsorbed species was followed from 30 to 600 °C. Peaks at ca. 3070 (not shown), 1600, 1530 (1504 for $\text{SiO}_2\text{-ZrO}_2$), 1490, 1440, and 1410 cm^{-1} appeared during the adsorption of toluene at 600 °C and remained in the spectrum of all the ZrO_2 -based catalysts during cooling in nitrogen to 30 °C (Fig. 6). The assignment of these peaks equals the assignments of the corresponding peaks in the higher temperatures of the TPA experiments. However, the peak at ca. 1600 cm^{-1} , although with very low intensity, might suggest formation of carbonaceous deposits on the catalysts. The significantly higher intensity of the peaks assigned to surface benzoates compared to the peak assigned to carbonaceous deposits is due to the higher extinction coefficient of C–O bonds in benzoates than that of C–C bonds in carbonaceous deposits.

During oxidation, the peak assigned to carbonaceous deposits disappeared above 300 °C from the spectra of the catalysts. The adsorbed benzoate species, on the other hand, vanished at temperatures above 400 °C from the spectrum of $\text{Y}_2\text{O}_3\text{-ZrO}_2$ and above 500 °C from the spectra of ZrO_2 and $\text{SiO}_2\text{-ZrO}_2$, indicating differing reactivity of benzoates toward oxygen between the catalyst samples. In addition, small new peaks in the range of 3000–2800 cm^{-1} (not shown) in the spectra of all ZrO_2 -based catalysts were observed during the heating of the samples in oxygen, which can be related to the rearranging of the adsorbed species before oxidation.

3.3.2. Gas-phase products during toluene TPO

The surface species that were irreversibly adsorbed on the surface of the ZrO_2 -based catalysts during the TPA experiments were oxidized in the TPO experiments by heating from ambient temperature to 600 °C under $\text{O}_2\text{/He}$ flow. The responses of O_2 , CO_2 , CO , H_2O , and H_2 were of interest here. Fig. 7 shows the evolution of CO_2 ($m/z=44$) and CO ($m/z=28$) and the consumption of oxygen ($m/z=32$) during the temperature-programmed oxidation over the studied catalysts. As indicated by the consumption of oxygen and the evolution of carbon oxides, the oxidation of carbonaceous surface species took place between 200 °C and 400 °C. The evolution of carbon oxides was intense during TPO, suggesting that the amount of retained carbonaceous deposits was notable, thus confirming the assumed carbon laydown at the high temperature part of the TPA run.

With ZrO_2 , one clear maximum was detected at approx. 330 °C for CO_2 and CO . Over $\text{Y}_2\text{O}_3\text{-ZrO}_2$ the formation of CO_2 and CO was detected at 325 °C and 335 °C, respectively. Another evolution of both carbon oxides occurred with $\text{Y}_2\text{O}_3\text{-ZrO}_2$ catalyst at approx. 400 °C. The formation of CO_2 over $\text{SiO}_2\text{-ZrO}_2$ was clearly lower in amount with higher T_{max} (maximum at 350 °C) than over the other catalysts (Fig. 7). Moreover, the total ratio of formed CO to CO_2 was highest over $\text{SiO}_2\text{-ZrO}_2$ and O_2 consumption was the lowest. T_{max} values (°C) for water during TPO were 340, 400, and 435 °C respectively for ZrO_2 , $\text{Y}_2\text{O}_3\text{-ZrO}_2$ and $\text{SiO}_2\text{-ZrO}_2$. The water curves again exhibited a similar shape and order of T_{max} values (°C) as in the TPA experiments (Fig. 5) with different catalysts. Hydrogen formation (not shown) was detected in trace amounts over all the catalysts during the temperature range of the main oxidation events, T_{max} values (°C) for H_2 on ZrO_2 , $\text{Y}_2\text{O}_3\text{-ZrO}_2$ and $\text{SiO}_2\text{-ZrO}_2$ being 355, 400, and 450 °C, respectively.

On ZrO_2 , the formation of all the oxidation products (CO_2 , CO , H_2 and H_2O) occurred at 330–355 °C (CO_2 and CO shown in Fig. 7). Over $\text{Y}_2\text{O}_3\text{-ZrO}_2$ and $\text{SiO}_2\text{-ZrO}_2$, on the other hand, the formation of H_2 and H_2O can be correlated with the additional formation of CO_2 and CO at higher temperature (a shoulder can be seen in

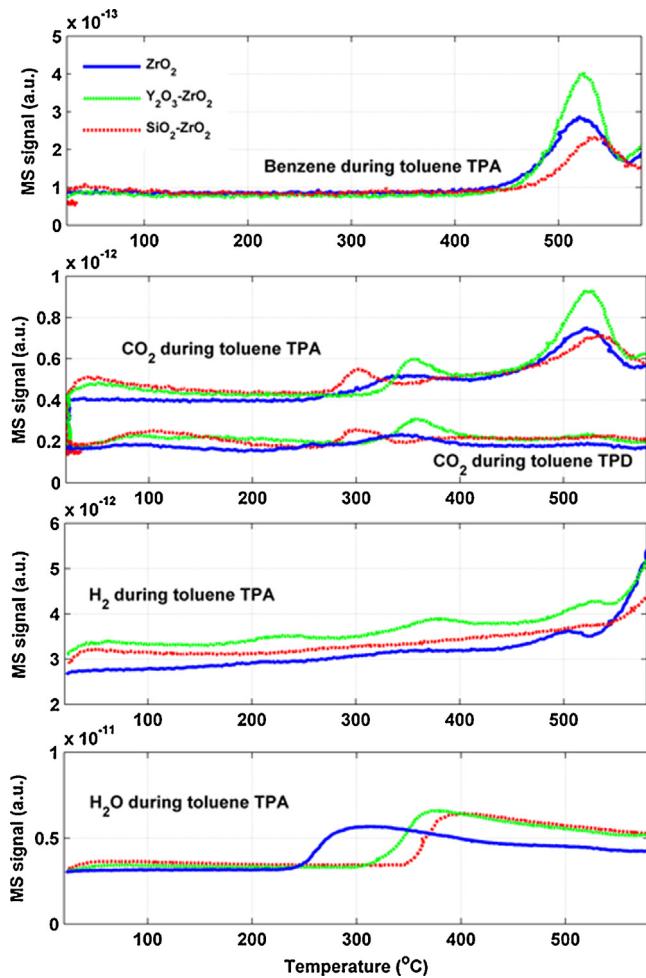


Fig. 5. MS signals for benzene, CO_2 , H_2 , and H_2O ($m/z = 78, 44, 2$, and 18 respectively) over ZrO_2 -based catalysts from ambient to 600°C during the toluene TPA experiments. CO_2 formation over all catalysts is also shown during the TPD experiments for comparison.

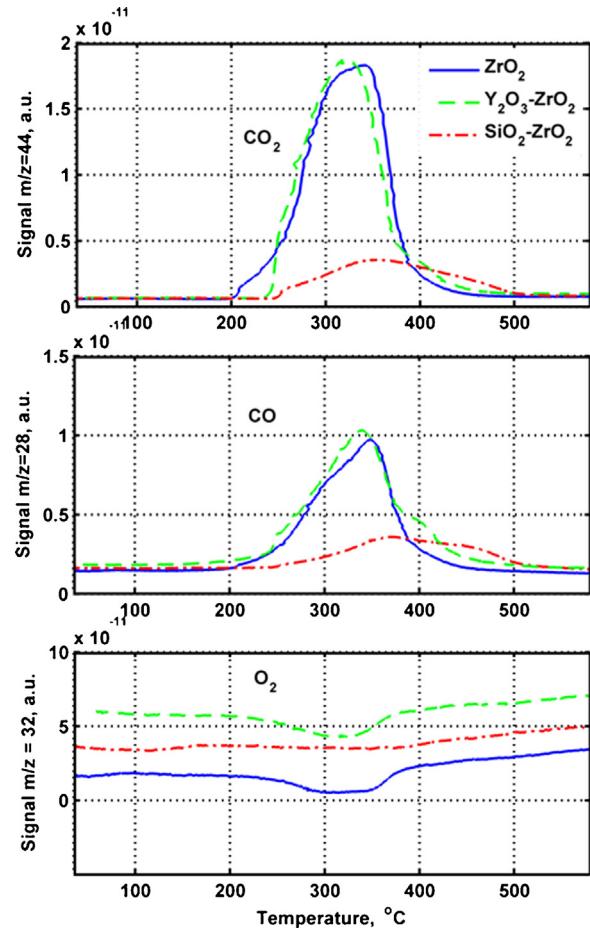


Fig. 7. CO_2 and CO formation and O_2 consumption (m/z values of 44 , 28 , and 32 respectively) from ambient to 600°C during the TPO-experiments.

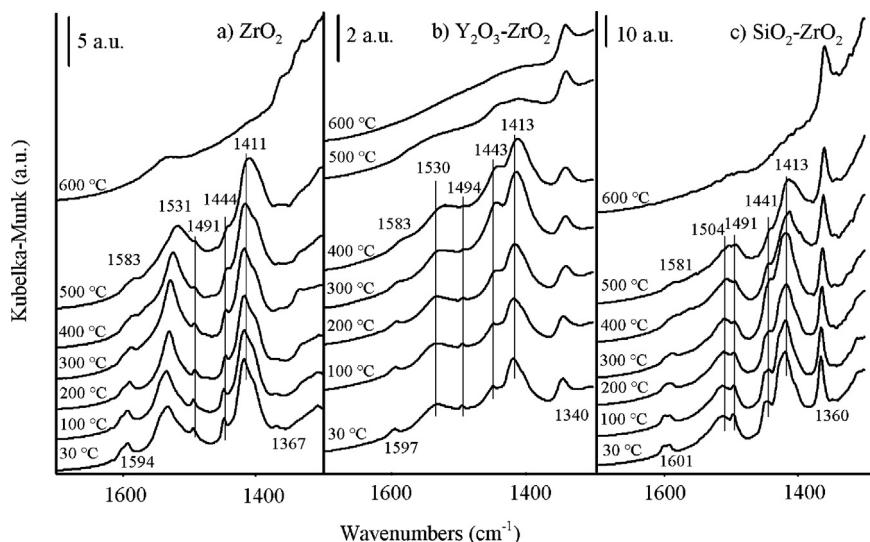


Fig. 6. DRIFTS spectra from the TPO experiments in the region of $1700\text{--}1300\text{ cm}^{-1}$ of calcined and reduced (a) ZrO_2 , (b) $\text{Y}_2\text{O}_3\text{-ZrO}_2$ and (c) $\text{SiO}_2\text{-ZrO}_2$ after toluene adsorption at 600°C and subsequent cooling to 30°C during oxidation from 30 to 600°C . All spectra were recorded under $2\% \text{O}_2/\text{N}_2$.

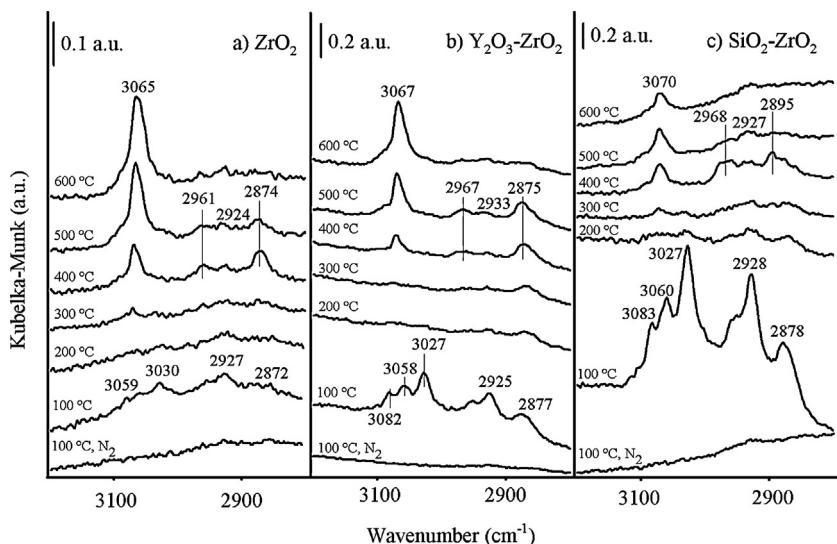


Fig. 8. DRIFTS spectra from the TPSR experiments in the region of 3200–2800 cm^{-1} of calcined and reduced (a) ZrO_2 , (b) $\text{Y}_2\text{O}_3\text{-ZrO}_2$ and (c) $\text{SiO}_2\text{-ZrO}_2$ during co-adsorption of toluene and oxygen from 100 to 600 $^\circ\text{C}$.

Fig. 7). Therefore, it is suggested that the carbonaceous deposits are more heterogeneous on the doped zirconias than on pure ZrO_2 .

3.4. Temperature-programmed surface reaction between toluene and oxygen (TPSR)

The co-adsorption of toluene and oxygen and their reactions were studied from 100 to 600 $^\circ\text{C}$ by in situ DRIFTS. Analogously to the TPD and the TPA experiments, molecularly adsorbed toluene species (peaks at ca. 3080, 3060, 3030, 2925, 2820, 1600, 1545 and 1490 cm^{-1}) were observed at low temperatures and adsorbed benzoate species (peaks at ca. 3070 (**Fig. 8**), 1510 and 1410 cm^{-1} (**Fig. S3** in Supplementary data)) at higher temperatures in the spectra of all the ZrO_2 -based catalysts. However, at temperatures above 300 $^\circ\text{C}$, new peaks compared to the toluene TPA experiments could be seen in the spectra of all the catalysts. The peaks at ca. 2960 and 2880 cm^{-1} in the spectra of all the catalysts above 300 $^\circ\text{C}$ can be assigned to the symmetric and asymmetric C–H stretching vibrations of a CH_2 group characteristic of benzyl species [21]. When toluene is adsorbed dissociatively giving one hydrogen atom from its methyl group, benzyl species are formed. Furthermore, the peaks at ca. 3070 and ca. 1580 cm^{-1} can be assigned to the skeleton vibrations of the aromatic ring of both benzyl and benzoate species [8,19]. Interestingly, only small, barely detectable benzyl peaks were detected in the reference TPA experiment where toluene was adsorbed on the calcined ZrO_2 , therefore suggesting that gas-phase oxygen increased the surface concentration of the benzyl species.

Supplementary data related to this article found, in the online version, at <http://dx.doi.org/10.1016/j.apcatb.2013.06.008>.

In the TPSR experiments, the gas flow from the DRIFTS cell was followed with an on-line mass spectrometer. As an example, the MS signals for the consumption of toluene and oxygen in the TPSR experiment over $\text{Y}_2\text{O}_3\text{-ZrO}_2$ are shown in **Fig. 9**. Over all the ZrO_2 -based catalysts, both toluene and oxygen started to convert at temperatures above 300 $^\circ\text{C}$ (shown for $\text{Y}_2\text{O}_3\text{-ZrO}_2$ in **Fig. 9**). The product formation was similar for all the ZrO_2 -based catalysts: water was formed below 300 $^\circ\text{C}$ due to desorption of physisorbed water and the oxidation products (CO_2 , CO , H_2O , and H_2) started to form above 300 $^\circ\text{C}$.

4. Discussion

4.1. Adsorption of toluene in the absence of gas-phase oxygen over ZrO_2 -based catalysts

Toluene adsorption in the absence of gas-phase oxygen was studied over ZrO_2 , $\text{Y}_2\text{O}_3\text{-ZrO}_2$, and $\text{SiO}_2\text{-ZrO}_2$. The low-temperature-adsorption of toluene resulted in molecularly adsorbed toluene on the surface of all the ZrO_2 -based catalysts (**Fig. 1**). Molecularly adsorbed toluene desorbed from the catalysts below 200 $^\circ\text{C}$ (**Figs. 1 and 2**). A similar relatively weak toluene adsorption mode that becomes unstable below 200 $^\circ\text{C}$ has been observed for a number of oxides [23,25]. The toluene curves in the TP experiments showed that the amount of toluene desorbing from the catalyst surface decreased in the order of $\text{SiO}_2\text{-ZrO}_2 > \text{Y}_2\text{O}_3\text{-ZrO}_2 > \text{ZrO}_2$ (**Fig. 2**). When the specific surface areas are taken into account, the amount of desorbed toluene in the TPD experiments was approximately 0.13, 0.23, and 0.23 $\mu\text{mol}/\text{m}^2_{\text{cat}}$ on ZrO_2 , $\text{Y}_2\text{O}_3\text{-ZrO}_2$, and $\text{SiO}_2\text{-ZrO}_2$, respectively. The total acidity and total basicity of these ZrO_2 -based catalysts (**Table 1**) have been measured in our previous work [7], but there is no clear correlation between toluene adsorption capacity and

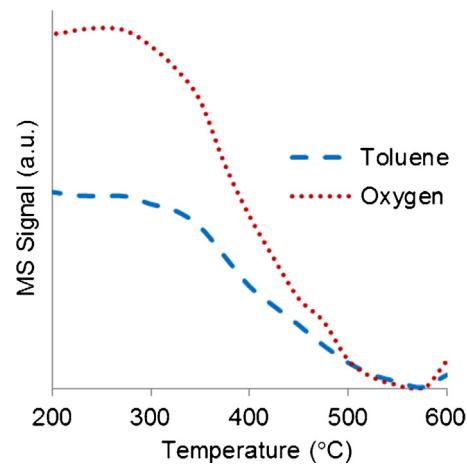


Fig. 9. Consumption of toluene and oxygen in the TPSR experiment over $\text{Y}_2\text{O}_3\text{-ZrO}_2$.

the acidity or the basicity of these catalysts. The differences in capacities per surface area for pure and doped zirconias obtained in this work are attributed to different chemical compositions that induce different crystalline phases of samples: pure ZrO_2 being monoclinic and doped samples containing tetragonal and cubic phases [7].

The adsorption of toluene in the absence of gas-phase oxygen (TPA experiments) revealed benzoate species on ZrO_2 as well as on $\text{SiO}_2\text{--ZrO}_2$ at temperatures above 300 °C and on $\text{Y}_2\text{O}_3\text{--ZrO}_2$ above 400 °C (Fig. 3). Benzoate species are formed when hydrogen is first abstracted from the methyl group of toluene and then a benzoate ion is formed using two surface oxygen atoms of the catalyst [8]. The analyses of gas-phase products during toluene adsorption in the absence of gas-phase oxygen showed that benzene and CO_2 were formed over all the catalysts at high temperatures of 525 °C (530 °C for $\text{SiO}_2\text{--ZrO}_2$) (Fig. 5). The temperature at which benzene and CO_2 were formed (Fig. 5) is higher than the temperature at which surface benzoate species started to appear in the spectra of the catalysts (Fig. 3). This suggests that some of the surface benzoate species undergo scission to benzene and CO_2 . This is also supported by the estimated equimolar amounts of CO_2 and benzene (approx. 0.1 $\mu\text{mol}/\text{m}^2$ for $\text{Y}_2\text{O}_3\text{--ZrO}_2$) produced, thus suggesting decarboxylation of surface benzoate species. The amount of O contained in the CO_2 detected corresponds roughly to 0.8% of surface oxygen atoms in the $\text{Y}_2\text{O}_3\text{--ZrO}_2$ surface. The small fraction of the surface oxygen species involved clearly indicated that minority sites like edge or corner sites are responsible, similar to the results of Zhu et al. [26], who reported somewhat higher amount of O removed from yttria-doped zirconia with methane at much higher temperature (900 °C). Furthermore, it may well be that surface OH groups are involved as a minority site, similar to the results of Jonson et al. [27], who reported that decarboxylation of benzoate species on $\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3\text{--C}$ catalysts benzene (and CO_2) requires OH groups of the catalyst surface.

Although the gasification gas mixture contains several compounds other than applied in this work, the role of surface benzoates species can be speculated. If toluene adsorbs as benzoates on the catalyst surface during gasification gas cleaning, the formation of unwanted side products is possible. Benzene formation via surface benzoates was detected during the TPA experiments (Figs. 3 and 5). Benzene has also been previously observed during gasification gas cleaning. Even though benzene is not classified as tar, its presence is not desired if the product gas is targeted, for example, at Fischer–Tropsch synthesis [6]. Furthermore, according to the literature, the ammonoxidation of toluene

goes through adsorbed surface benzoates that react with ammonia (ammonia is always present in the gasification gas) to benzonitrile [28]. Benzonitrile has previously been detected during gasification gas cleaning over ZrO_2 -based catalysts [28]. Benzonitrile is a harmful compound and is also classified as tar, thus an undesirable component in the product gas.

4.2. Oxidation of toluene-derived surface species

Essential information on the oxidation of toluene-derived species was gathered in the TPO experiments, where residual carbon-containing species that originate from toluene adsorption were removed from the surface of the catalysts by oxidation. The major formation of oxidation products in the gas phase was observed at approx. 330 °C (Fig. 5), whereas the surface benzoate species vanished from the spectrum of $\text{Y}_2\text{O}_3\text{--ZrO}_2$ above 400 °C and from the spectra of ZrO_2 and $\text{SiO}_2\text{--ZrO}_2$ above 500 °C (Fig. 3). Therefore, it seems that benzoate species are not responsible for the major formation of oxidation products. However, the small peak at ca. 1600 cm^{-1} tentatively assigned to carbonaceous deposits disappeared from the spectra of all the catalysts above 300 °C (Fig. 3), thus suggesting that it could be related to the major formation of oxidation products detected in the gas phase (Fig. 5) at the temperature in question. The fact that surface benzoate species are more stable than the carbonaceous deposits toward oxygen seems to be surprising at first sight but is actually expected, since adsorbed benzoate species have been reported to be highly stable according to Hernández-Alonso et al. [19]. In the TPO experiments, the formation of CO_2 and CO started at a lower temperature over ZrO_2 and $\text{Y}_2\text{O}_3\text{--ZrO}_2$ than over $\text{SiO}_2\text{--ZrO}_2$ (Fig. 7). Furthermore, it is evident that the carbonaceous deposits on the doped zirconias are more heterogeneous than on pure ZrO_2 based on the TPO results; over pure ZrO_2 the carbon on the surface was oxidized in one step, whereas on the doped zirconias two events could be distinguished (Fig. 7).

The simultaneous adsorption of toluene and oxygen showed yet another surface species on ZrO_2 -based catalysts that was not observed in any other experiments; at temperatures above 300 °C benzyl species appeared in the spectra (Fig. 8). Benzyl species are formed from toluene when one hydrogen atom from the methyl group is abstracted and toluene is adsorbed via the methylene group ($-\text{CH}_2$) on the surface of the catalyst [21]. At temperatures above 300 °C, the consumption of both toluene and oxygen was initiated and increased with increasing temperature (Fig. 9). The temperature where consumption of toluene and oxygen started

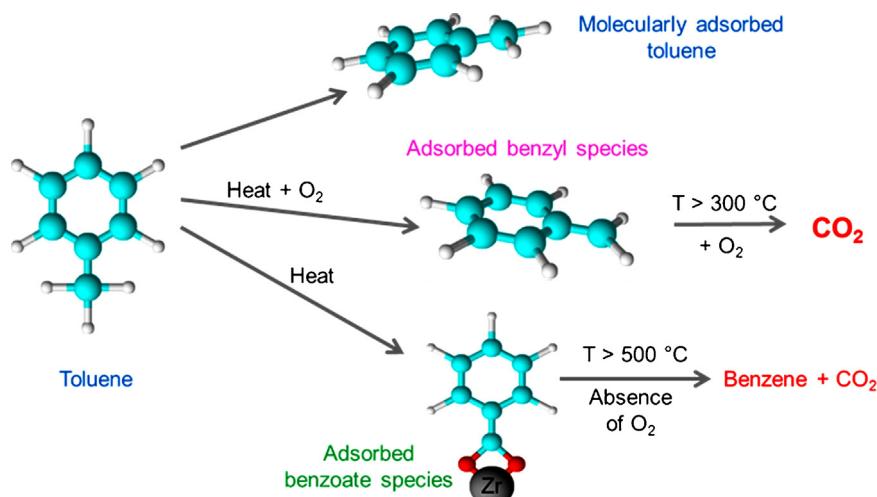


Fig. 10. Schematic presentation of the mechanistic steps involved in the adsorption and oxidation of toluene over ZrO_2 -based gasification gas clean-up catalysts.

(Fig. 9) correlates well with the formation temperature of the surface benzyl species (Fig. 8). Furthermore, at higher temperatures (above 500 °C) where the consumption of toluene and oxygen started to stabilize (Fig. 9), the surface benzyl species vanished from the spectrum (Fig. 8). The surface benzoate species, on the other hand, showed evidently strong peaks in the spectra of ZrO₂-based catalysts still at 600 °C (Fig. 8). Of all the surface species that were derived from toluene, benzoates were also found to be least reactive toward oxygen. Therefore, it can be suggested that the surface benzoate species are spectator species in toluene oxidation, similar to the finding of Paulis et al. [16], who observed that benzoate species became spectators in the total oxidation of toluene over Pd/Al₂O₃ catalyst as well. Furthermore, the surface benzyl species seem to be the intermediate of the toluene oxidation reaction over ZrO₂-based catalysts, similar to the postulation of Busca [29] for several vanadia catalysts (partial oxidation) as well as for α -Fe₂O₃ (total oxidation).

5. Conclusions

The interaction of toluene with selected ZrO₂-based gasification gas clean-up catalysts in the absence and presence of gas-phase oxygen was studied with two complementary techniques: in situ DRIFTS and temperature-programmed gas-phase analysis. The combination of these two techniques offered unique knowledge on the adsorbed surface species from toluene as well as information on their decomposition and/or oxidation mechanisms over ZrO₂, Y₂O₃–ZrO₂, and SiO₂–ZrO₂. Using this knowledge, the nature of the adsorbed toluene-derived surface species (the mechanistic steps are shown schematically in Fig. 10) over ZrO₂-based gasification gas clean-up catalysts could thus be evaluated.

The adsorption of toluene in the absence of gas-phase oxygen leads to three types of surface species over ZrO₂-based gasification gas clean-up catalysts: molecularly adsorbed toluene, surface benzoate species, and carbonaceous deposits. Molecularly adsorbed toluene desorbs at low temperatures without reacting. Surface benzoate species are formed when toluene adsorbs on the ZrO₂-based catalysts at temperatures above 400 °C. In the absence of gas-phase oxygen, some of the benzoate species decompose into benzene and CO₂ corresponding roughly to a removal of 0.8% ML of surface oxygen atoms from the surface of Y₂O₃–ZrO₂.

When toluene and oxygen are co-fed to ZrO₂-based catalysts, the presence of benzyl species can be detected. The benzyl species appear to the spectra of all ZrO₂-based catalysts at the same temperature where toluene and oxygen start to convert and oxidation products (CO₂, CO, H₂O and H₂) start to form. However, at higher temperatures (above 500 °C) where the consumption of toluene and oxygen started to stabilize, the surface benzyl species vanished from the spectrum. The surface benzoate species, on the other hand, were still present at 600 °C, indicating strong adsorption of these species. Therefore, it is suggested that the highly stable surface benzoate species are spectators, while the surface benzyl species seem to be a key intermediate in the toluene oxidation reaction.

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